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**DETAILED DESCRIPTION**

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**[Detailed Description of the Invention]****[0001]**

[Field of the Invention] This invention is a constituent for paint containing polysilazane, and relates to the coating structure formed of the constituent for construction paint which can form a tough coat especially in a building wall surface etc., its coating method, and it.

**[0002]**

[Description of the Prior Art] As a constituent for polysilazane content coat formation, conventionally, The constituent for coating containing the poly metalaw silazane produced by making carry out the pyrogenetic reaction of polysilazane and the metal alkoxide (JP,1-221466,A), The constituent for coating containing the silicon alkoxide addition poly metalaw silazane produced by making carry out the pyrogenetic reaction of polysilazane and the silicon alkoxide (JP,5-238827,A), The coating composition containing the glycidol addition poly metalaw silazane produced by making carry out the pyrogenetic reaction of polysilazane and the glycidol (JP,6-122852,A), The coating composition containing the alcoholic addition poly metalaw silazane produced by making carry out the pyrogenetic reaction of polysilazane and the alcohol (JP,6-240208,A), The coating composition (JP,6-299118,A) and polysilazane containing \*\*\*\*\*\*, and the general formula  $(CH_3 COCHCOCH_3)_n M$  which are produced by making various metal carboxylate react to polysilazane The coating composition (JP,6-306329,A) containing the acetylacetonato complex addition polysilazane produced by [M making carry out the pyrogenetic reaction of the acetylacetonato complex of the various metal shown by n-valent metal], etc. are indicated.

[0003] These polysilazane content coating compositions, It can excel in heat resistance, abrasion resistance, and chemical resistance, moreover a tunic with high surface hardness can be formed, it can calcinate at low temperature comparatively more further, and the thing containing especially perhydropolysilazane has an advantageous point which can be stiffened

without calcination at ordinary temperature.

[0004]However, if it is in the coating composition which blended oxidation catalysts, such as metal carboxylate and an acetylacetonato complex, with perhydropolysilazane, If field painting is performed since activity is very high while it can be made to harden without calcination at ordinary temperature as mentioned above, That is, when brush coating, spray coating, etc. were performed under ordinary temperature and an air atmosphere, it reacted to the moisture in the atmosphere, oxygen, etc. violently, in the case of spray coating, the main part of a spray gun caused blinding in the inside of a short time, and there was a problem where coating work becomes impossible despite a join office. In this case, although it was possible to use the special coating system devised so that it might not be influenced by moisture or oxygen, it became expensive in price to use such a special coating system for the field painting in a construction site, and it was not realistic.

[0005]Then, the 1st purpose of this invention can be stiffened in ordinary temperature and the atmosphere that the above problems should be canceled, without calcinating, And yet even if it does not use a special coating system, it is in providing the constituent for perhydropolysilazane content construction paint which can perform field painting, such as brush coating and spray coating, into the atmosphere.

[0006]On the other hand, its attention is paid to the semiconductor particulate (henceforth "photocatalyst grains") which carries out optical functional catalyses, such as titanium oxide, and various uses, such as sterilization of these various semiconductor particulates, deodorization, decloudy weather, and washing, have been indicated in recent years. For example, if titanium oxide is made to adhere to the surfaces, such as a sound insulating wall of a road, an outer wall of a building, and a telephone booth, a self cleaning function can be given to these surfaces.

[0007]As a method of making it adhere to the object surface, such photocatalyst grains, The method of making the object surface supporting photocatalyst grains in JP,9-164091,A etc. using an organic binder, Photocatalyst grains are applied to the method which applies the precursor of the photocatalyst to the object surface and can be printed at around 600 \*\*, and also the heated object surface made from a plastic, and the method of pressing with a metallic mold etc. and laying photocatalyst grains underground, etc. are indicated.

[0008]However, the method of using an organic binder had SUBJECT that it was short-life, in order for the organic binder of the photocatalyst-grains circumference to decompose by a photocatalyst effect, to lose a binder function and for a photocatalyst to be omitted from a substrate. It was impossible to have applied the method which can be printed at around 600 \*\* to the wall surface of a building as a matter of fact, and in order that the method of laying the above-mentioned photocatalyst grains underground might also heat the object surface beforehand, the construction to the wall surface of a building was actually difficult.

[0009]Then, the 2nd purpose of this invention does not use an organic binder that the above problems should be canceled, And photocatalyst grains can be made to adhere to the object surface, without calcinating, and it is in providing the constituent for polysilazane content construction paint which can form a photocatalyst activity tunic tough on especially the wall surface of a building, and long-life by field painting.

[0010]

[Means for Solving the Problem]For this purpose achievement, although this invention persons diluted to a limit which can be assumed as a usual paint and tried spray painting in the atmosphere first in a constituent for coat formation which blends perhydropolysilazane and an oxidation catalyst with an organic solvent, a main part of a spray gun caused blinding. Although a combination presentation, such as adding various additive agents, was changed and tried also after that, it could be made to harden in ordinary temperature and the atmosphere, and a result which can perform field painting simply in the atmosphere was not obtained. However, as a result of doing a thinned constituent and trying about this to such an extent that it could not assume as a usual paint by chance, unbelievably it could be made to harden in ordinary temperature and the atmosphere, and discovered that field painting could moreover be simply performed in the atmosphere. This invention is made based on this knowledge.

[0011]Namely, an invention of claim 1 is an organic solvent, polysilazane, and an oxidation catalyst which do not have OH opportunity a constituent for construction paint to contain, and as the polysilazane concerned, It is a constituent for construction paint blending perhydropolysilazane (number average molecular weights 100-50,000) which does not have an organic group 0.1 to 5% of the weight by solids concentration conversion, and an invention of claim 2 blends photocatalyst grains during a presentation of this constituent for construction paint. It is a coating method, wherein an invention of claim 3 applies the above-mentioned constituent for construction paint by paint of a brush, a paint roller, a spray, etc., and an invention of claim 4 is coating structure which applies the above-mentioned constituent for construction paint to a thickness of 0.01 micrometer - 1 micrometer.

[0012]

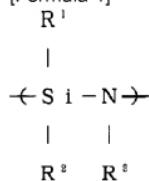
[Embodiment of the Invention]Hereafter, the suitable embodiment in this invention is described.

[0013]The constituent for construction paint of this invention can blend "polysilazane" and an "oxidation catalyst" with a "solvent", can prepare a polysilazane solution, and can dilute and manufacture this with a "solvent" further. Although explained in accordance with this manufacturing method below, diluting to prescribed concentration at once is also possible, without not limiting the process of the constituent for construction paint of this invention to this, and using the "solvent" concerned.

[0014]in the following chemical formula in which the "polysilazane" used by this invention shows polysilazane -- both R1 R2 and R3 -- although -- it is perhydropolysilazane which is a hydrogen atom. Since all having combined with Si or N are H, not only like steric exclusion not barring a reaction small but like an organic group, oxidize the perhydropolysilazane which does not have an organic group and it is not decomposed. Therefore, only by holding in ordinary temperature and the atmosphere, oxidation or hydrolysis by the water vapor of the air progresses, and it hardens, and since it moreover functions as a perfect minerals binder, a photocatalyst effect cannot decompose and a long-life photocatalyst activity tunic can be formed. The molecular weight in particular of perhydropolysilazane is not limited and it is [ molecular weight ] usable in the thing of the number average molecular weights 100-50,000.

[0015]

[Formula 1]



[0016]As an "oxidation catalyst" used by this invention, it is the general formula (RCOO) nM in metal carboxylate and the concrete target which are indicated in the [0024] columns of JP,6-299118,A. It is shown by n-valent metal] and [M is metal. [M]Carry out and For example, nickel, titanium, platinum, rhodium, cobalt, iron, a ruthenium, What [ has at least a kind of metal chosen from groups, such as osmium palladium, iridium, and aluminum, ], It is an acetylacetone complex of the various metal currently indicated in the [0023] columns of JP,6-306329,A, and the complex which the negative ion specifically produced from the acetylacetone (2, 4-pentadione) by acid dissociation configurated in the metal atom, and is the general formula (CH<sub>3</sub> COCHCOCH<sub>3</sub>) n M. It is shown by n-valent metal] and [M is metal. [M] What carries out, for example, has nickel, platinum, palladium, aluminum, rhodium, etc. can be mentioned. However, it is not limited to these. the loadings of an "oxidation catalyst" -- an oxidation catalyst / polysilazane polymerization ratio -- 0.000001-2 -- desirable -- 0.001-1 -- it adds so that it may be set to 0.01-0.5 still more preferably.

[0017]In a "solvent" used by this invention, aromatic hydrocarbon, aliphatic hydrocarbon, A hydrocarbon solvent of alicyclic hydrocarbon, halogenated hydrocarbon, aliphatic series ether, An organic solvent which are alicycle fellows ether, aromatic amine, etc. and does not have an OH radical, for example, benzene, toluene, xylene, a methylene chloride, chloroform, n-hexane, ethyl ether, a tetrahydrofuran, pyridine, methylpyridine, etc. are used. It limits to an

organic solvent which does not have an OH radical in this invention in order to prevent a reaction of a solvent and polysilazane.

[0018]As a "solvent" used by this invention, an organic solvent illustrated as a solvent, i.e., an organic solvent which does not have an OH radical, can be used conveniently.

[0019]Although a constituent for construction paint of this invention blends the above "polysilazane" and the above "oxidation catalyst" above a "solvent", prepares a polysilazane solution, can dilute this polysilazane solution above a "solvent" and can create it further, At this time, a blending ratio of "perhydropolysilazane" is adjusted so that it may be preferably contained 0.1 to 3% of the weight 0.1 to 5% of the weight as solids concentration in a solvent thru/or a solvent. If it increases more than 5 % of the weight, field painting in inside of the atmosphere will become impossible instantly, and if less than 0.1 % of the weight, a function will fall extremely as a binder. It is indicated that a result to adjust to the [0031] columns of JP,6-299118,A and the [0031] columns of JP,6-306329,A in the range whose solvent concentration is 0 to 90 % of the weight is obtained, And in a constituent for construction paint used for a use of construction, considering film thickness and concentration of a formed element being less than 10% was usually being unable to think at all. However, in this invention, it succeeded in acquiring an effect peculiar to this invention by daring to adjust that to 5 or less % of the weight.

[0020]"Photocatalyst grains" can be blended with the above-mentioned combination presentation, and a photocatalyst effect can be given to a coat.

[0021]As "photocatalyst grains", titanium oxide (TiO<sub>2</sub>), iron oxide (Fe<sub>2</sub>O<sub>3</sub>), Particles of a photocatalyst known conventionally [, such as tungstic oxide (WO<sub>1</sub>), a zinc oxide (ZnO), zinc sulfide (ZnS), a cadmium sulfide (CdS), titanic acid straw CHIUMU (SrTiO<sub>2</sub>), and a molybdenum sulfide (MoS<sub>2</sub>), ] can be used.

[0022]Although these "photocatalyst grains" is also directly mixable in the above-mentioned polysilazane solution, In order to make homogeneity distribute photocatalyst grains more, apart from a polysilazane solution M-xylene, A dispersing agent is mixed to various organic solvents, such as o-xylene, photocatalyst grains are mixed to this, particulate dispersion liquid can be adjusted, this particulate dispersion liquid and the above-mentioned polysilazane solution can be mixed, and a constituent for construction paint can be created. As a "dispersing agent", SORUSU pass #3000 by Zeneka Co., #9000, and #17000 are mentioned, for example, and #9000 and #17000 are used preferably here. As for quantity of this dispersing agent, 5 to 50 % of the weight is preferred to photocatalyst grains, and its 10 to 30 % of the weight is especially preferred.

[0023]Hereafter, an execution method in a case of applying to a facing wall of a building is explained as an example of an execution method of a constituent for construction paint of this invention.

[0024]First, although it is then if needed, in advance of paint of polysilazane, washing work is performed using a high-pressure-washing machine etc. to a paint object face, and a paint object face is thoroughly dried through air-dry care of health after an appropriate time.

[0025]Then, next, a created constituent for construction paint is applied to an external wall surface of a building by field painting, such as spray coating, like the above. Although it is not necessary to use a special coating system devised so that it might not be influenced by moisture or oxygen especially as a spray device, If an electrostatic-coating machine or a high volume low pressure spray which suits not less than 65% of application efficiency, and 0.1 psi of atomization air pressure - 10 psi (0.007-0.7 kg/cm<sup>2</sup>) standard is used, there is no blinding more and it can apply to homogeneity more.

[0026]At this time, as for especially quantity that applies a constituent for construction paint, when blending photocatalyst grains, it is preferred to apply to a thickness of 0.01 micrometer - 1 micrometer. If it is called film thickness for construction, since it will usually be 30 micrometers - 50 micrometers, usually assume, and are \*\*\*\*\* thickness, but. The tunic surfaces can certainly be made scattered and, moreover, photocatalyst grains with a particle diameter of 0.01 micrometer - 1 micrometer can be made to adhere to an external wall surface certainly by forming in 0.01 micrometer - 1 micrometer of film thickness. In the surface for paint, the raw materials in particular, such as various metal and concretes and glass, or various plastics, are not limited.

[0027]A constituent for construction paint applied in this way by allowing to stand at a room temperature in the air for one to three days, Oxidation is promoted by oxidation catalyst, perhydropolysilazane in a constituent is hardened according to it, and a Si-O system which a photocatalyst distributed, or Si-N-O system ceramics, i.e., a precise and tough tunic of perfect inorganic matter, are formed in the surface. It excels in corrosion resistance, heat resistance, and abrasion resistance, this tunic has high adhesion on the surface of an object, and since tunics are moreover perfect minerals, it does not decompose and deteriorate with a photocatalyst.

[0028]When the photocatalyst concerned receives light of wavelength with energy more than a band cap, for example, sunlight and light of an electric light, by making photocatalysts scattered on the surface, An electron which has a reducing action strong against the surface by optical pumping, and an electron hole with strong oxidation are produced, and a self cleaning function which decomposes and removes quality of dirty things, such as an organic substance which adhered to the surface by these oxidation reduction operations, and oil, is exhibited. The patent No. 2756474 is indicating a view of making the surface carrying out chemical absorption in a form of a hydroxyl group (OH-), carrying out hydrophilization of the base material surface, and giving a self cleaning function to the surface by a photocatalyst effect of a photocatalyst. In for example, the case of a constituent for paints which makes a

silicone paint come to distribute photocatalyst grains. Hydrophilization of the object surface (if it puts in another way silicone paint surface as a binder) itself is carried out by making an organic group combined with a silicon atom of a silicone molecule replace by a hydroxyl group by a photocatalyst effect. On the other hand, since what uses perhydropolysilazane which does not have an organic group and does not have an OH radical as a solvent and a solvent is used for this invention, it completely differs from thought of the patent No. 2756474 of carrying out hydrophilization of the tunic surface itself by a photocatalyst effect. Incidentally, although the patent No. 2756474 is indicating use of polysilazane, it limits to an ORGANO polysilazane compound which has an organic group. A difference among both is clear also from this point.

[0029]

[Example]Hereafter, the example of this invention is described.

[0030](1) Dissolve the perhydropolysilazane (inorganic polysilazane) which does not have a manufacture organic group of the constituent for construction paint, and propionic acid palladium (C2 H5 COOPd) in a m-xylene solution, and a polysilazane solution is prepared 20% of the weight, This was further diluted with the m-xylene solution, and the constituent for construction paint of each combination (combination 1-4) of the following table 1 was manufactured.

[0031]

[Table 1]

配合	配合 1	配合 2	配合 3	配合 4
20重量%ポリシラザン溶液	100	100	100	100
m-キシレン	0	100	300	500
固形分濃度(重量%)	20	10	5	3.3

[0032](2) 100g of constituents for coat formation of the brush coating paint above-mentioned combination 1-4 were measured to the poly cup container, and the work which uses the common brush for a metal plate and is applied at a rate of 10-20 g/m<sup>2</sup> of coverage was done. Work was done under 20 \*\* and 65% of environment, time until material reacts to oxygen in the air or moisture and it interferes with brush coating work in this case was made into working limit time, and the test result was shown in Table 2.

[0033]

[Table 2]

	配合例 1	配合例 2	配合例 3	配合例 4
作業開始時間(分)	10分	20分	60分以上	60分以上
ボリカップ中の材料の状況	7~8分後 ゲル化	15分後 ゲル化	塗装終了まで 以上なし	塗装終了まで 以上なし
塗装状況	ゲル化により 10分以上作業できない	ゲル化により 20分以上作業できない	通常作業に 支障なし	通常作業に 支障なし
実用性の判定	実用的でない	実用的でない	実用上問題無	実用上問題無

[0034]As a result, by the time working hours pass 10 minutes or 20 minutes about the combination 1 and 2, gelling will already have started in the container, and coating work beyond this was not completed. On the other hand, about the combination 3 and 4, gelling of material was not produced till the end of coating work (for about 30 minutes), but the usual coating work without coating nonuniformity was able to be performed.

[0035](3) 100g of constituents for construction paint of the paint-roller paint above-mentioned combination 1-4 were measured to the poly cup container, and the work which uses a paint roller for a metal plate and is applied at a rate of 10-20 g/m<sup>2</sup> of coverage was done. Work was done under 20 \*\* and 65% of environment, time until material reacts to oxygen in the air or moisture and it interferes with brush coating work in this case was made into working limit time, and the test result was shown in Table 3.

[0036]

[Table 3]

	配合例 1	配合例 2	配合例 3	配合例 4
作業開始時間(分)	10分	20分	60分以上	60分以上
ボリカップ中の材料の状況	7~8分後 ゲル化	15分後 ゲル化	塗装終了まで 以上なし	塗装終了まで 以上なし
塗装状況	ゲル化により 10分以上作業できない	ゲル化により 20分以上作業できない	通常作業に 支障なし	通常作業に 支障なし
実用性の判定	実用的でない	実用的でない	実用上問題無	実用上問題無

[0037]As a result, by the time working hours pass 10 minutes or 20 minutes about the combination 1 and 2, gelling will already have started in the container, and coating work beyond this was not completed. On the other hand, about the combination 3 and 4, gelling of material was not produced till the end of coating work (for about 30 minutes), but the usual coating work without coating nonuniformity was able to be performed.

[0038](4) After carrying out the SUPU paint during 1 minute for the constituent for construction paint of the spray painting above-mentioned combination 1-4 by an air spray gun using an air

spray gun, the process of carrying out a pause for 30 seconds was repeated, and coating work was performed. The setting-out / paint conditions of the used air spray gun are as follows. nozzle diameter: -- 0.6mm spraying air pressure: -- 3.0 kg/cm<sup>2</sup> air-consumption: -- 30 l. / min spraying distance: -- 200mm paint jetting volume: -- 30 ml / min movement speed: -- about 20 - cm/min pattern difference: -- 100-mm work 20 \*\*, It carried out under 65% of environment, the number of times until material reacts to oxygen in the air or moisture and it interferes with coating work in this case was measured, this was made into the rule of thumb of the time which can be painted, and the test result was shown in Table 4.

[0039]

[Table 4]

	配合例 1	配合例 2	配合例 3	配合例 4
繰り返し回数	2回	5回	異常なし	異常なし
塗装可能時間	2～8分	5～10分	60分以上	60分以上
塗装状況	2回目に塗装時にノズル詰まりが発生	5回目に塗装時にノズル詰まりが発生	材料がなくなまるまで異常なし	材料がなくなまるまで異常なし
実用性の判定	実用的でない	実用的でない	実用的である	実用的である

[0040]As a result, about the combination 1 and 2, the appearance of material worsened under the influence of nozzle plugging by two to five paint-pauses, and it changed into the state where it cannot spray any more from causes, like liquid sagging arises from the cancer point. on the other hand -- until all the prepared constituents are lost about the combination 3 and 4 (for about 15 minutes) -- up to -- the state at the time of a spray start was maintained.

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[Translation done.]